

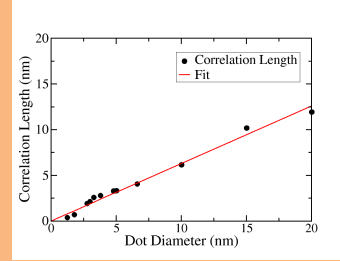
Determination of electron-hole correlation length in CdSe quantum dots using explicitly correlated two-particle cumulant

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ABSTRACT: The electron-hole correlation length serves as an intrinsic length scale for analyzing excitonic interactions in semiconductor nanoparticles. In this work, the derivation of electron-hole correlation length using the two-particle reduced density is presented. The correlation length was obtained by first calculating the electron-hole cumulant from the pair density, and then transforming the cumulant into intracuclear coordinates, and finally then imposing exact sum-rule conditions on the radial integral of the cumulant. The excitonic wave function for the calculation was obtained variationally using the electron-hole explicitly correlated Hartree-Fock method. As a consequence, both the pair density and the cumulant were explicit functions of the electron-hole separation distance. The use of explicitly correlated wave function and the integral sum-rule condition are the two key features of this derivation. The method was applied to a series of CdSe quantum dots with diameters 1-20 nm and the effect of dot size on the correlation length was analyzed.



Keywords: explicitly correlated, Gaussian-type geminal, electron-hole correlation, reduced density matrix, cumulant, transition density matrix

I. Introduction

Electron-hole excitations in semiconductor quantum dots are influenced by their size, shape and chemical composition. Controlling the generation and the dissociation of electron-hole (eh) pairs have important technological applications in the field of light-harvesting materials[1–4], photovoltaics[5–8], solid-state lighting[9–12] and lasing[13–16]. In order to control the generation and dissociation of the eh-pair, it is important to understand the underlying interaction between the quasiparticles. Theoretical treatment of electron-hole interaction in quantum dots is challenging because of the computational bottleneck associated with quantum mechanical treatment of many-electron systems. In principle, a simplified description of the electron-hole pair can be achieved by ignoring the eh interaction and treating them as independent quasiparticles. Although this approach can dramatically reduce the computational cost, such simplification can lead to qualitatively wrong results. For example, optical spectra calculation using independent quasiparticle approach often shows significant deviation from the experimental results. One of the main limitations of the independent quasiparticle method is its inability in describing bound excitonic states. Multiexcitonic interaction, exciton and biexciton binding energies, radiative and Auger recombination

are some of the properties whose calculations depend on the accurate treatment of electron-hole correlation. Theoretical investigation of electron-hole correlation has been performed using various methods such as time-dependent density functional theory (TDDFT)[17–24], perturbation theory[25], GW combined with Bethe-Salpeter equation[26–34], configuration interaction[35–43], quantum Monte Carlo[38, 44–46], path-integral Monte Carlo,[47, 48] explicitly correlated Hartree-Fock method,[49–53] and electron-hole density functional theory.[54]

In this work, we are interested in the calculation of electron-hole correlation length (eh-CL) in CdSe quantum dots. Our goal is to provide a statistical definition of the electron-hole correlation length. The concept of correlation length has been widely used in many fields, including statistical mechanics[55–58] and polymer science.[56–62] One of the important features of the eh-CL is that it provides an intrinsic length scale for describing the electron-hole interaction. Because of this, it can play an important role in describing excitonic effects in quantum dots and other nanomaterials such as carbon nanotubes.[63–65] The eh-CL can also be used for construction of electron-hole correlation functional for multicomponent density functional theory.[54] For example, Salahub and co-workers have developed a series of exchange-correlation functions that are based on electron-electron correlation length[66–69] and a similar strategy can be used for construction of electron-hole correlation functionals using eh-CL. The eh-CL can also aid in the development of explicitly correlated wave functions (such as Jastrow and Gaussian-type geminal functions) which depend directly on the electron-hole separation distance.[46, 49–53]

We have used the 2-particle electron-hole density matrix

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for the definition and calculation of the eh-CL. Two-particle reduced density matrix (2-RDM) has been used extensively for investigation of electron-electron correlation[71–77] and electronic excitation[78] in many-electron systems. For the present system, the 2-RDM is the appropriate mathematical quantity that contains all the necessary information about electron-hole correlation. Specifically, the cumulant associated with the electron-hole 2-RDM is the component of the 2-RDM that cannot be expressed as a product of 1-particle electron and hole densities. In principle, the 2-RDM can be obtained directly without the need for an underlying wave function as long as the N -representability of 2-RDM can be satisfied. However, in the present work, we have obtained the 2-RDM from an explicitly correlated electron-hole wave function. The remainder of the article is organized as follows. The derivation of eh-CL from the electron-hole cumulant is presented in [subsection II A](#), transformation to intracule and extracule coordinates is described in [subsection II B](#), and details of the explicitly correlated electron-hole wave function are presented in [subsection II C](#) and [section III](#). The method was applied to a series of CdSe quantum dots and the results are presented in [section IV](#).

II. Theory

A. Electron-hole cumulant

The interaction between the quasiparticles in the quantum dot is described the electron-hole Hamiltonian[36–38, 46, 49, 50, 52, 53, 80–87] which has the following general expression

$$\begin{aligned} H = & \sum_{ij} \langle i | \frac{-\hbar^2}{2m_e} \nabla_e^2 + v_{\text{ext}}^e | j \rangle e_i^\dagger e_j \\ & + \sum_{ij} \langle i | \frac{-\hbar^2}{2m_h} \nabla_h^2 + v_{\text{ext}}^h | j \rangle h_i^\dagger h_j \\ & + \sum_{ij i' j'} \langle ij i' j' | \varepsilon^{-1} r_{eh}^{-1} | ij i' j' \rangle e_i^\dagger e_j h_{i'}^\dagger h_{j'} \\ & + \sum_{ijkl} w_{ijkl}^{ee} e_i^\dagger e_j^\dagger e_l e_k + \sum_{ijkl} w_{ijkl}^{hh} h_i^\dagger h_j^\dagger h_l h_k. \end{aligned} \quad (1)$$

We define the electron-hole wave function for a multiexcitonic system consisting of N_e and N_h number of electrons and holes, respectively by $\Psi_{eh}(\mathbf{x}_1^e, \dots, \mathbf{x}_{N_e}^e, \mathbf{x}_1^h, \dots, \mathbf{x}_{N_h}^h)$, where \mathbf{x} is a compact notation for both the spatial and spin coordinate of the particles. The spin-integrated 2-particle reduced density can be obtained from the electron-hole wave function by integration over the $N_e - 1$ and $N_h - 1$ coordinates as shown in the following equation

$$\rho_{eh}(\mathbf{r}^e, \mathbf{r}^h) = \frac{N_e N_h}{\langle \Psi_{eh} | \Psi_{eh} \rangle} \int ds_1^e ds_1^h d\mathbf{x}_2^e, \dots, \mathbf{x}_{N_e}^e \mathbf{x}_2^h, \dots, \mathbf{x}_{N_h}^h \Psi_{eh}^* \Psi_{eh} \quad (2)$$

where, integration over the spin coordinate s_1 is performed for both electron and hole. The single-particle density is obtained from the 2-particle density using the sum-rule condition[70]

$$\rho_e(\mathbf{r}^e) = \frac{1}{N_h} \int d\mathbf{r}^h \rho_{eh}(\mathbf{r}^e, \mathbf{r}^h), \quad (3)$$

$$\rho_h(\mathbf{r}^h) = \frac{1}{N_e} \int d\mathbf{r}^e \rho_{eh}(\mathbf{r}^e, \mathbf{r}^h). \quad (4)$$

We define the electron-hole cumulant as the difference between the 2-particle density and the product of the 1-particle electron and hole densities as shown in the following equation

$$q(\mathbf{r}^e, \mathbf{r}^h) = \rho_{eh}(\mathbf{r}^e, \mathbf{r}^h) - \rho_e(\mathbf{r}^e) \rho_h(\mathbf{r}^h). \quad (5)$$

This definition is analogous to the definition used by Mazzionti et al.[88] in electronic structure theory. By construction, the cumulant contains information about correlation between the two particles. Consequently, the Coulomb contribution of the electron-hole correlation energy can be directly expressed in terms of the electron-hole cumulant and is given by the following expression

$$\begin{aligned} \langle \Psi_{eh} | V_{eh} | \Psi_{eh} \rangle &= \langle \rho_{eh} \varepsilon^{-1} r_{eh}^{-1} \rangle \\ &= J_{eh} + \langle q(\mathbf{r}^e, \mathbf{r}^h) \varepsilon^{-1} r_{eh}^{-1} \rangle, \end{aligned} \quad (6)$$

where ε is the dielectric constant and J_{eh} is the classical Coulomb electron-hole energy

$$J_{eh} = \langle \rho_e \rho_h \varepsilon^{-1} r_{eh}^{-1} \rangle. \quad (7)$$

The cumulant has an important property that its integration over all space should be zero due to the density sum-rule conditions[70]

$$\int d\mathbf{r}^e d\mathbf{r}^h q(\mathbf{r}^e, \mathbf{r}^h) = 0. \quad (8)$$

We use this relationship for the definition of the electron-hole correlation length.

B. Intracule and extracule coordinates

Beginning with Coleman's initial definition of the intracule and extracule matrices in terms of the center of mass (extracule) and relative motion (intracule) coordinates,[89] the concept of the intracule and extracule in the regime of electronic systems has been previously explored in earlier studies.[89–95] The intracule and extracule coordinates for the eh-system are defined by

$$\mathbf{r}_{eh} = \mathbf{r}^e - \mathbf{r}^h \quad (9)$$

$$\mathbf{R} = \frac{1}{2} (\mathbf{r}^e + \mathbf{r}^h). \quad (10)$$

The integral of the cumulant is expressed in terms of these coordinates

$$\int d\mathbf{r}^e d\mathbf{r}^h q(\mathbf{r}^e, \mathbf{r}^h) = \int d\mathbf{r}_{eh} \int d\mathbf{R} q(\mathbf{r}_{eh}, \mathbf{R}) \quad (11)$$

$$= \int_0^\infty dr_{eh} r_{eh}^2 \int d\Omega \sin \theta \int d\mathbf{R} q(\mathbf{r}_{eh}, \mathbf{R}) \quad (12)$$

$$= \int_0^\infty dr_{eh} r_{eh}^2 q_r(r_{eh}) \quad (13)$$

In the above expression, the integral over the intracuclear coordinate \mathbf{r}_{eh} is transformed into spherical polar coordinates. The function q_r is the spherically averaged radial cumulant and the integral of the radial cumulant over a finite limit is used to define the following function $I(d)$

$$I(d) = \int_0^d dr_{\text{eh}} r_{\text{eh}}^2 q_r(r_{\text{eh}}). \quad (14)$$

The zero-integral property of q (defined in Eq. (8)) ensures that this integral goes to zero at large d

$$\lim_{d \rightarrow \infty} I(d) = 0. \quad (15)$$

Here, we use $I(d)$ to define the electron-hole correlation length. Specifically, the electron-hole correlation length (r_c) is defined as the value of d at which the value of $I(d)$ is zero

$$|I(r_c)| = 0 \quad r_c < \infty. \quad (16)$$

The description of the electron-hole wave function used for the calculation of the radial cumulant is presented in the following section.

C. Explicitly correlated electron-hole wave function

We have used the electron-hole explicitly correlated Hartree-Fock method (eh-XCHF) for obtaining the electron-hole wave function. This method has been used in earlier work for the computation of exciton binding energies and electron-hole recombination probabilities in quantum dots.[49–53] A brief summary of the eh-XCHF method is presented here and the implementation details of this method can be found in work by Elward and co-workers.[50–52] The ansatz of the eh-XCHF wave function consists of multiplying the mean-field electron-hole reference wave functions with an explicitly correlated function G as shown in the following equation

$$\Psi_{\text{eh-XCHF}} = G\Phi_e\Phi_h, \quad (17)$$

where G is the geminal operator

$$G = \sum_{i=1}^{N_e} \sum_{j=1}^{N_h} g(r_{ij}), \quad (18)$$

$$g(r_{\text{eh}}) = \sum_{k=1}^{N_g} b_k \exp(-\gamma_k r_{\text{eh}}^2). \quad (19)$$

The eh-XCHF method is a variational method in which the correlation function G and the reference wave function are obtained by minimizing the total energy

$$E_{\text{eh-XCHF}} = \min_{G, \Phi_e, \Phi_h} \frac{\langle G\Phi_0 | H | G\Phi_0 \rangle}{\langle G\Phi_0 | G\Phi_0 \rangle}, \quad (20)$$

where $\Phi_0 = \Phi_e\Phi_h$. To perform the above minimization, it is more efficient to work with the following congruent-transformed operators

$$\tilde{H} = G^\dagger H G, \quad (21)$$

$$\tilde{I} = G^\dagger G. \quad (22)$$

This transformation is particularly important for the calculation of the 2-particle reduced density matrix in the present work. The set of parameters $\{b_k, \gamma_k\}$ in G were obtained by non-linear optimization, and for a given set of these parameters, the minimization over the reference wave function was performed by determining the self-consistent solution of the coupled Fock equations

$$\tilde{\mathbf{F}}_e \mathbf{C}_e = \tilde{\mathbf{S}}_e \mathbf{C}_e \lambda_e, \quad (23)$$

$$\tilde{\mathbf{F}}_h \mathbf{C}_h = \tilde{\mathbf{S}}_h \mathbf{C}_h \lambda_h. \quad (24)$$

The tilde in the above expressions represent that the Fock and the overlap matrices incorporate the transformed operators defined in Eq. (21).

The transformed operator \tilde{I} can be written as a sum of operators as shown below

$$\tilde{I} = G^\dagger G \quad (25)$$

$$= \sum_{ii'} g(i, i') \sum_{jj'} g(j, j') \quad (i, j = 1, \dots, N_e; i', j' = 1, \dots, N_h) \quad (26)$$

$$= \sum_{ii'} g(i, i') g(i, i') + \sum_{i \neq j, i'} g(i, i') g(j, i') \quad (27)$$

$$+ \sum_{i' \neq j', i} g(i, i') g(i, j') + \sum_{i \neq j, i' \neq j'} g(i, i') g(j, j').$$

The above expression can be written in a compact notation as a sum of 2, 3, and 4-particle operators

$$G^\dagger G = \Omega_{11} + \Omega_{21} + \Omega_{12} + \Omega_{22}. \quad (28)$$

The 2-particle density for the eh-XCHF wave function can be expressed in terms of these operators as shown below

$$\rho_{\text{eh}}(\mathbf{r}^e, \mathbf{r}^h) = \frac{N_e N_h}{\langle \Psi_{\text{eh-XCHF}} | \Psi_{\text{eh-XCHF}} \rangle} \times \langle \Psi_{\text{eh-XCHF}}^* \Psi_{\text{eh-XCHF}} \rangle_{s_1, s'_1, 2, 2', \dots, N_e, N_h}, \quad (29)$$

where the subscript in the above expression is a compact notation for integration over the remaining coordinates described in Eq. (2). Substituting the expression from Eq. (28), we get the following expression

$$\rho_{\text{eh}}(\mathbf{r}^e, \mathbf{r}^h) = \frac{N_e N_h}{\langle \Phi_0 | \tilde{I} | \Phi_0 \rangle} \times \langle \Phi_0^* (\Omega_{11} + \Omega_{12} + \Omega_{21} + \Omega_{22}) \Phi_0 \rangle_{s_1, s'_1, 2, 2', \dots, N_e, N_h}. \quad (30)$$

For a multiexcitonic system all 2, 3, and 4-particle operators should be used for the computation of the 2-particle density. In a related work on many-electron system, we have shown that it is possible to avoid integration over higher-order operators by using diagrammatic summation technique and a similar strategy can be used for multiexcitonic systems as well.[96]

D. Relation to uncorrelated transition density matrices

One of the important features of the correlation function is that it allows for a compact representation of the 2-particle density matrix in the position representation. The relationship can be readily seen by expanding the eh-XCHF wave function in the Slater determinant basis

$$G\Phi_0 = \sum_{ii'} \underbrace{\langle \Phi_i^e \Phi_{i'}^h | G | \Phi_0^e \Phi_0^h \rangle}_{c_{ii'}} \Phi_i^e \Phi_{i'}^h = \sum_{ii'} c_{ii'} \Phi_i^e \Phi_{i'}^h. \quad (31)$$

Substituting Eq. (31) in the expression of ρ_{eh} gives

$$\begin{aligned} \rho_{eh}(\mathbf{r}^e, \mathbf{r}^h) &= \frac{N_e N_h}{\langle \Phi_0 | \tilde{I} | \Phi_0 \rangle} \\ &\times \left(\sum_{ij} \sum_{i'j'} c_{ii'}^* c_{jj'} \Phi_i^{e*} \Phi_{i'}^{h*} \Phi_j^e \Phi_{j'}^h \right)_{s_1, s_1', 2, 2', \dots, N_e, N_h} \\ &= \frac{N_e N_h}{\langle \Phi_0 | \tilde{I} | \Phi_0 \rangle} \sum_{ij} \sum_{i'j'} c_{ii'}^* c_{jj'} d_{ij}^e d_{i'j'}^h, \end{aligned} \quad (32)$$

where the transition density matrix d_{ij} is defined as

$$d_{ij}^e(\mathbf{r}^e) = \langle \Phi_i^{e*} \Phi_j^e \rangle_{s_1, 2, \dots, N_e}. \quad (33)$$

It is seen from Eq. (32) that the 2-particle density obtained from the eh-XCHF wave function is equivalent to the infinite-order expansion in terms of the transition density matrices.

III. Computational details

The method described in section II was used for calculating electron-hole correlation length in CdSe quantum dots in the range of 1-20 nm in diameter. We are interested in the effect of dot size on the electron-hole correlation length for a single electron-hole pair in CdSe quantum dots. For a single electron-hole pair, the higher-order operators in Eq. (30) rigorously vanish from the expression. This provides considerable simplification in the calculation of the 2-particle density. Because of the dot size, application of either DFT or atom-centered pseudopotential approach is computationally prohibitive. To make the computation tractable, we have used a parabolic confining potential in the electron-hole Hamiltonian described in Eq. (1). Parabolic confinement potential in quantum dots has been used extensively for various properties such as total exciton energy[97, 98], exciton dissociation[99], exciton binding energy[49, 50, 52, 100] eh-recombination probability[49–51], effect of magnetic[101–106] and electric fields[53, 101, 107–109], exciton-polariton condensate[110], linear optical properties[111, 112], optical rectification[113], non-linear rectification[107], dynamics[114], eh-correlation energy[115, 116], resonant tunneling[117], collective modes[118], and thermodynamic properties[119]. The external potential for the electron and hole quasiparticle was defined as

$$v_\alpha^{\text{ext}} = \frac{1}{2} k_\alpha |\mathbf{r}_\alpha|^2 \quad \alpha = e, h \quad (35)$$

TABLE I. Force constants for CdSe quantum dots.

Dot diameter (nm)	k_e (atomic units)	k_h (atomic units)
1.24	2.66×10^{-2}	9.10×10^{-3}
1.79	6.22×10^{-3}	2.13×10^{-3}
2.76	1.10×10^{-3}	3.76×10^{-4}
2.98	8.10×10^{-4}	2.77×10^{-4}
3.28	5.52×10^{-4}	1.89×10^{-4}
3.79	3.09×10^{-4}	1.06×10^{-4}
4.80	1.20×10^{-4}	4.12×10^{-5}
5.00	1.02×10^{-4}	3.51×10^{-5}
6.60	3.40×10^{-5}	1.16×10^{-5}
10.00	6.41×10^{-6}	2.19×10^{-6}
15.00	1.26×10^{-6}	4.33×10^{-7}
20.00	4.01×10^{-7}	1.37×10^{-7}

where k_α is the force constant which determines the strength of the confinement potential. We have used a particle-number based search procedure for determination of the force constant k_α . The central idea of this approach is to find the value of k_α such that the computed 1-particle electron and hole densities are confined within the volume of the quantum dot. This is obtained by performing the following minimization

$$\min_{k_\alpha^{\text{min}}} \left(N_\alpha - \int_0^{\frac{D_{\text{dot}}}{2}} dr r^2 \int d\Omega \rho_\alpha(\mathbf{r}) \right)^2, \quad (36)$$

where D_{dot} is the diameter of the quantum dot and Ω is the angular coordinate. The values of the force constants used for each dot is listed in Table I. The kinetic energy operator was computed using the electron and hole effective masses of 0.13 and 0.38 atomic units, respectively.[81] The interaction between the electron and hole was described by screened Coulomb potential. We have used the size and distance dependent dielectric function $\epsilon(\mathbf{r}, R_{\text{dot}})$, which was developed by Wang and Zunger for CdSe.[120] The electron and hole molecular orbitals in Φ_0 were represented using a linear combination of Gaussian type orbitals (GTOs) and the expansion coefficients were obtained by the solving the coupled Fock equations shown in Eq. (23). The basis used was a single S Cartesian GTO was used and the exponents of the basis functions are listed in Table II. The use of GTOs is especially convenient because the integrals involving the GTOs and the Gaussian correlation function, G , are known analytically.[121–124] For a given value of \mathbf{r}^e , the 1-particle density ρ was calculated analytically. The integration over the intracuclear coordinate in Eq. (14) was performed numerically. The correlation function, G , was expanded as a linear combination of six Gaussian-type geminal functions[49, 50, 52] and the set of $\{b_k, \gamma_k\}$ parameters were optimized for each dot size. The first set of geminal parameters was set to $b_1 = 1$ and $\gamma_1 = 0$ for all CdSe dot diameters. For each dot diameter, five sets of geminal parameters were determined sequentially by minimizing the energy. The values of the geminal parameters are found in Table III.

TABLE II. Exponent used in GTO basis $e^{-\alpha r^2}$.

Dot diameter (nm)	α (atomic units)
1.24	2.94×10^{-2}
1.78	1.42×10^{-2}
2.76	5.98×10^{-2}
2.98	5.13×10^{-2}
3.28	4.24×10^{-3}
3.79	3.17×10^{-3}
4.80	1.98×10^{-3}
5.00	1.83×10^{-3}
6.60	1.05×10^{-3}
10.00	4.57×10^{-4}
15.00	2.03×10^{-4}
20.00	1.14×10^{-4}

IV. Results

The electron-hole correlation length was obtained by integration of the radial cumulant as described in Eq. (14). In Figure 1, the integral of the cumulant, $I(d)$, for three different dot sizes are presented. As expected, the integral goes to zero

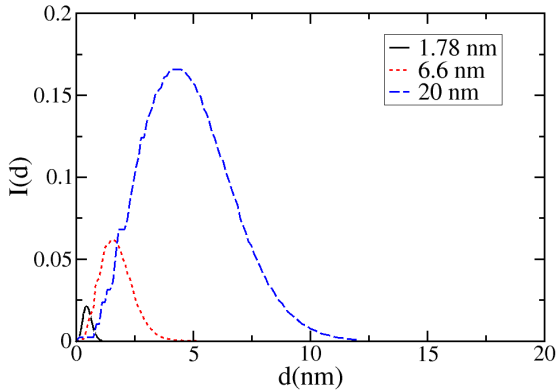


FIG. 1. The value of $I(d)$ as d , the upper limit in Eq. (14), is varied for the 1.78 nm, 6.6 nm, and 20 nm diameter CdSe quantum dots.

at large distances (high d values) and the distance at which the integral converges to zero is defined as the electron-hole correlation length r_c . The calculated electron-hole correlation lengths are presented in Table IV. We find that, in all cases, the correlation length increases with increasing dot diameter. Another quantity that is important for investigating electron-hole correlation is the length scale associated with the first node of the radial cumulant. We define this quantity as r_{node} and the calculated values are presented in Table IV. The maximum of the $I(d)$ in Figure 1 corresponds to r_{node} . Because the interaction between the electron and hole is attractive, we expect an enhancement in the pair density as compared to mean-field density at small r_{eh} distances. This

phenomenon is opposite to the correlation hole observed in electron-electron interaction, in which small r_{ee} shows a decrease in correlated electron-pair density as compared to uncorrelated electron density. The r_{node} can be interpreted as the effective radius of the sphere that encloses the region of enhanced probability density. As seen from Table IV, r_c and r_{node} are similar in magnitude for small dot sizes, but these quantities differ significantly for larger dots. The correlation length as a function of the dot diameter is plotted in Figure 2. The set of data showed good agreement with the linear fit, with a mean absolute error of 0.323 nm. A trend of increasing correlation length with increasing dot diameter is observed. The correlation lengths show that correlation effects are important even at long electron-hole separations. The linear re-

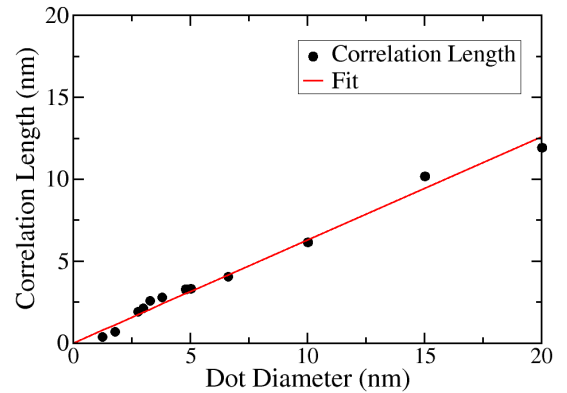


FIG. 2. The correlation length as a function of the dot diameter D_{dot} . The linear fit is $r_c = 0.6303D_{\text{dot}}$, with a mean absolute error of 0.323 nm.

lationship between the dot diameter and the correlation length has an important application in the construction of compact explicitly correlated electron-hole wave function. For example, the determination of the eh-XCHF wave function requires the optimization of the non-linear parameters $\{b_k, \gamma_k\}$ in G . By using the relationship between the dot diameter and correlation length, it is possible to assign the non-linear parameters as some multiple of the correlation length. This approach avoids optimization of non-linear parameters and can result in significant reduction in the computational effort.

V. Conclusions

In conclusion, we have presented a method for calculating electron-hole correlation length in semiconductor quantum dots. We have used the cumulant derived from the electron-hole 2-particle density as the central quantity for defining the correlation length. There are two key features of this method. First, the 2-particle reduced density was obtained from an explicitly correlated electron-hole wave function. Consequently, the reduced density matrix and the corresponding cumulant

TABLE III. Value of the geminal parameters for CdSe quantum dots.

Dot Diameter (nm)	b_2	γ_2	b_3	γ_3	b_4	γ_4	b_5	γ_5	b_6	γ_6
1.25	1.338×10^{-1}	2.134×10^{-2}	1.559×10^{-1}	1.150×10^{-3}	3.630×10^{-2}	1.112×10^0	2.290×10^{-2}	2.111×10^{-1}	1.099×10^{-1}	1.020×10^{-3}
1.78	1.497×10^{-1}	1.569×10^{-2}	2.099×10^{-1}	1.120×10^{-3}	2.009×10^{-1}	4.400×10^{-4}	4.260×10^{-2}	1.112×10^0	3.820×10^{-2}	1.444×10^{-1}
2.76	2.279×10^{-1}	4.700×10^{-3}	5.990×10^{-2}	1.111×10^{-1}	2.119×10^{-1}	4.400×10^{-4}	-1.910×10^{-2}	3.140×10^{-3}	1.540×10^{-2}	1.222×10^0
2.98	2.449×10^{-1}	3.960×10^{-3}	6.400×10^{-2}	1.114×10^{-1}	2.099×10^{-1}	3.700×10^{-4}	1.490×10^{-2}	1.434×10^0	1.580×10^{-2}	1.012×10^{-1}
3.28	2.589×10^{-1}	3.580×10^{-3}	6.680×10^{-2}	1.112×10^{-1}	2.109×10^{-1}	4.300×10^{-4}	9.990×10^{-2}	1.100×10^{-4}	1.590×10^{-2}	1.253×10^0
3.79	2.799×10^{-1}	3.000×10^{-3}	6.990×10^{-2}	1.111×10^{-1}	2.209×10^{-1}	3.700×10^{-4}	1.099×10^{-1}	1.200×10^{-4}	1.540×10^{-2}	1.432×10^0
4.80	3.610×10^{-1}	1.660×10^{-3}	8.790×10^{-2}	1.010×10^{-1}	6.180×10^{-2}	2.229×10^{-2}	2.099×10^{-1}	2.200×10^{-4}	9.990×10^{-2}	1.100×10^{-4}
5.00	3.699×10^{-1}	1.570×10^{-3}	8.990×10^{-2}	1.010×10^{-1}	6.680×10^{-2}	2.135×10^{-2}	2.099×10^{-1}	2.200×10^{-4}	9.990×10^{-2}	1.100×10^{-4}
6.60	4.499×10^{-1}	1.380×10^{-3}	6.099×10^{-1}	1.800×10^{-4}	5.280×10^{-2}	1.112×10^0	1.299×10^{-1}	1.011×10^{-1}	1.331×10^{-1}	1.335×10^{-2}
10.00	5.899×10^{-1}	1.240×10^{-3}	9.999×10^{-1}	1.300×10^{-4}	6.400×10^{-2}	1.012×10^0	1.569×10^{-1}	1.023×10^{-1}	1.799×10^{-1}	1.211×10^{-2}
15.00	6.999×10^{-1}	1.040×10^{-3}	1.110×10^0	1.300×10^{-4}	6.580×10^{-2}	1.102×10^0	1.589×10^{-1}	1.022×10^{-1}	1.999×10^{-1}	1.999×10^{-1}
20.00	7.999×10^{-1}	1.030×10^{-3}	2.000×10^0	1.200×10^{-4}	9.999×10^{-1}	4.000×10^{-5}	5.489×10^{-1}	1.227×10^{-2}	2.899×10^{-1}	1.240×10^{-3}

TABLE IV. Electron-hole correlation lengths and r_{node} for CdSe quantum dots.

Dot Diameter (nm)	Correlation length (nm)	r_{node} (nm)
1.24	0.381	0.283
1.78	0.683	0.431
2.76	1.905	0.595
2.98	2.117	0.653
3.28	2.572	0.732
3.79	2.778	0.833
4.80	3.293	1.082
5.00	3.307	1.124
6.60	4.047	1.653
10.00	6.156	2.749
15.00	10.164	3.257
20.00	11.930	4.733

were explicit functions of the electron-hole separation distance. Second, the calculation of the correlation length was not based on the nodes of the cumulant but was derived from the exact sum rule relationship satisfied by all N -representable cumulants. The developed method was applied to a series of CdSe quantum dots and a linear relationship between the dot size and correlation length was observed. The electron-hole correlation length provides a natural length scale for investigating electron-hole correlation in nanoparticles. We envision that in future work, the electron-hole correlation length will be used in the construction of compact explicitly correlated wave functions and also for developing multi-component[54] electron-hole density functionals.

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